

## EAST Search History

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	101108	cyclopropyl acetylenes	US-PGPUB; USPAT; EPO; DERWENT	OR	ON	2007/01/08 13:56
L2	49	L1 and 1,3-butadiyne	US-PGPUB; USPAT; EPO; DERWENT	OR	ON	2007/01/08 13:57
L3	50896	dicyclopropyl acetylenes	US-PGPUB; USPAT; EPO; DERWENT	OR	ON	2007/01/08 13:57
L4	0	1,4-dicyclopropyl-1,3-butadiyne	US-PGPUB; USPAT; EPO; DERWENT	OR	ON	2007/01/08 13:57
L5	373	dicyclopropyl butadiyne	US-PGPUB; USPAT; EPO; DERWENT	OR	ON	2007/01/08 13:58
L6	315	CPA.clm.	US-PGPUB; USPAT; EPO; DERWENT	OR	ON	2007/01/08 13:59
L7	91	TMEDA.clm.	US-PGPUB; USPAT; EPO; DERWENT	OR	ON	2007/01/08 13:58
L8	0	L6 and L7	US-PGPUB; USPAT; EPO; DERWENT	OR	ON	2007/01/08 13:58
L9	1355650	copper chloride	US-PGPUB; USPAT; EPO; DERWENT	OR	ON	2007/01/08 13:59
L10	71191	L1 and L9	US-PGPUB; USPAT; EPO; DERWENT	OR	ON	2007/01/08 14:00
L11	20	L10 and L7	US-PGPUB; USPAT; EPO; DERWENT	OR	ON	2007/01/08 14:00
L12	972385	substituted butadiynes	US-PGPUB; USPAT; EPO; DERWENT	OR	ON	2007/01/08 14:00

## EAST Search History

L13	67550	L12 and L1	US-PGPUB; USPAT; EPO; DERWENT	OR	ON	2007/01/08 14:01
L14	21272	L13 and L3	US-PGPUB; USPAT; EPO; DERWENT	OR	ON	2007/01/08 14:01
L15	247	L14 and L5	US-PGPUB; USPAT; EPO; DERWENT	OR	ON	2007/01/08 14:01
S1	0	1,4-dicyclopropyl-1,3-butadiyne	US-PGPUB; USPAT; EPO; DERWENT	OR	ON	2006/09/12 15:23
S2	70	1,3-butadiyne	US-PGPUB; USPAT; EPO; DERWENT	OR	ON	2006/09/11 16:56
S3	1	1,4-substituted-1,3-butadiyne	US-PGPUB; USPAT; EPO; DERWENT	OR	ON	2006/09/11 16:56
S4	2	"7083690"	US-PGPUB; USPAT; EPO; DERWENT	OR	ON	2006/09/11 18:04
S5	78	585/534	US-PGPUB; USPAT; EPO; DERWENT	OR	ON	2006/09/12 11:29
S6	29	585/505	US-PGPUB; USPAT; EPO; DERWENT	OR	ON	2006/09/12 11:29
S7	2	"7049295"	US-PGPUB; USPAT; EPO; DERWENT	OR	ON	2007/01/08 13:55

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FILE 'HOME' ENTERED AT 14:03:51 ON 08 JAN 2007

=> file reg

COST IN U.S. DOLLARS

SINCE FILE  
ENTRY

TOTAL  
SESSION

FULL ESTIMATED COST

0.21

0.21

FILE 'REGISTRY' ENTERED AT 14:04:03 ON 08 JAN 2007

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DICTIONARY FILE UPDATES: 7 JAN 2007 HIGHEST RN 916885-50-2

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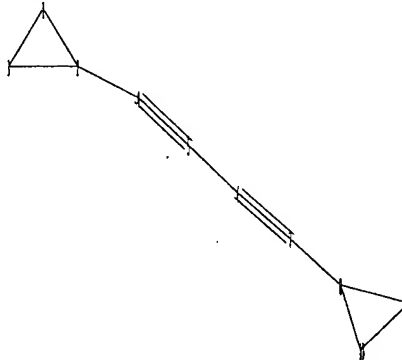
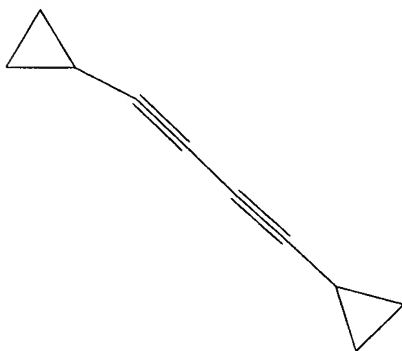
<http://www.cas.org/ONLINE/UG/regprops.html>

=> ....Testing the current file.... screen

ENTER SCREEN EXPRESSION OR (END):end

=>

Uploading C:\Program Files\Stnexp\Queries\10817411amdt.str



```

chain nodes :
4 5 6 7
ring nodes :
1 2 3 8 9 10
chain bonds :
2-4 4-5 5-6 6-7 7-8
ring bonds :
1-2 1-3 2-3 8-9 8-10 9-10
exact/norm bonds :
1-2 1-3 2-3 8-9 8-10 9-10
exact bonds :
2-4 4-5 5-6 6-7 7-8

```

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Match level :
1:CLASS 2:CLASS 3:CLASS 4:Atom 5:Atom 6:Atom 7:Atom 8:CLASS 9:CLASS
10:CLASS

```

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L1      STRUCTURE UPLOADED
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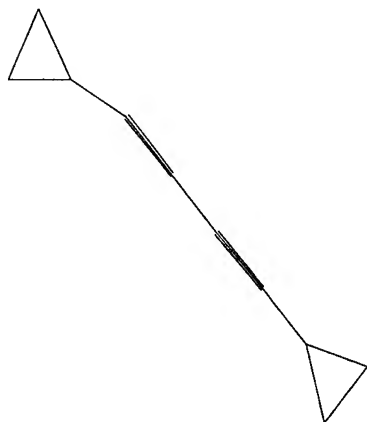
```
=> que L1
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```
L2      QUE L1
```

```
=> d L1
```

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L1 HAS NO ANSWERS
```

```
L1      STR
```



Structure attributes must be viewed using STN Express query preparation.

```
=> s L1 full
```

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FULL SEARCH INITIATED 14:04:30 FILE 'REGISTRY'
```

```
FULL SCREEN SEARCH COMPLETED - 9152 TO ITERATE
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```
100.0% PROCESSED 9152 ITERATIONS
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38 ANSWERS
```

```
SEARCH TIME: 00.00.01
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```
L3      38 SEA SSS FUL L1
```

```
=> file caplus
```

```
COST IN U.S. DOLLARS
```

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SINCE FILE
```

```
TOTAL
```

```
ENTRY
```

```
SESSION
```

```
FULL ESTIMATED COST
```

```
172.10
```

```
172.31
```

FILE 'CAPLUS' ENTERED AT 14:04:36 ON 08 JAN 2007  
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FILE LAST UPDATED: 7 Jan 2007 (20070107/ED)

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=> s L3

L4 24 L3

=> d L4 1-24 bib abs

L4 ANSWER 1 OF 24 CAPLUS COPYRIGHT 2007 ACS on STN  
AN 2006:759293 CAPLUS  
DN 145:314315  
TI Many Density Functional Theory Approaches Fail To Give Reliable Large Hydrocarbon Isomer Energy Differences  
AU Schreiner, Peter R.; Fokin, Andrey A.; Pascal, Robert A., Jr.; De Meijere, Armin  
CS Institute of Organic Chemistry, Justus-Liebig University Giessen, Giessen, 35392, Germany  
SO Organic Letters (2006), 8(17), 3635-3638  
CODEN: ORLEF7; ISSN: 1523-7060  
PB American Chemical Society  
DT Journal  
LA English  
AB Several DFT methods were found to be unreliable for computing hydrocarbon isomer energy differences. The errors grow with system size up to 20 kcal mol<sup>-1</sup> for the relative energies of the (CH)<sub>12</sub> isomers; octahedrane is the most stable (CH)<sub>12</sub> hydrocarbon. While DFT geometries generally are good, problems arise for structures with single bonds only, especially for small rings. We recommend the use of higher level, non-DFT energy single points computed at DFT-optimized structures.  
RE.CNT 23 THERE ARE 23 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 2 OF 24 CAPLUS COPYRIGHT 2007 ACS on STN  
AN 2003:42223 CAPLUS  
DN 138:109213  
TI Metal carboxylate-amine complexes as catalysts for imparting hypergolicity to rocket fuels in presence of hydrogen peroxide  
IN Dobbins, Thomas A.; Wiley, David B.  
PA Wiley Organics, Inc., USA  
SO PCT Int. Appl., 17 pp.  
CODEN: PIXXD2  
DT Patent  
LA English

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	WO 2003004443	A2	20030116	WO 2002-US20587	20020627
	WO 2003004443	A3	20031016		
	W:				
	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW				
	RW:				
	GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
	US 2003015268	A1	20030123	US 2002-180210	20020626
	US 7083690	B2	20060801		
	GB 2392442	A	20040303	GB 2004-257	20020627
	GB 2392442	B	20051012		
PRAI	US 2001-302729P	P	20010703		
	US 2001-344715P	P	20011024		
	WO 2002-US20587	W	20020627		

AB Self-ignition catalysts for rocket alc. or hydrocarbon propellants (e.g., MeOH or kerosene), which impart hypergolicity to the fuel in the presence of rocket fuel-grade hydrogen peroxide, consist of complexes of a metal carboxylate salt (or a metal 1,3-dione chelate) with an alkyl-substituted diamine or triamine. Suitable components of the complexes are: (1) Mn, Co, Cu, and Ag (as the metal), (2) acetates, propionates, and butyrates (as the carboxylate), (3) acetylacetone, 2,4-pentanedione, 3,5-heptanedione (as the 1,3-dione), and (4) 1,3-pentanediamine, N,N-dimethylethylenediamine, N,N,N',N'-tetramethylenediamine, and N,N,N',N'-tetramethyl-1,3-butanediamine. Suitable components of the complexes are: (1) Mn, Co, Cu, and Ag (as the metal), (2) acetates, propionates, and butyrates (as the carboxylate), (3) acetylacetone, 2,4-pentanedione, 3,5-heptanedione (as the 1,3-dione), and (4) 1,3-pentanediamine, N,N-dimethylethylenediamine, N,N,N',N'-tetramethylenediamine, and N,N,N',N'-tetramethyl-1,3-butanediamine. The hypergolicity-imparting catalyst is synthesized and isolated prior to adding it to the organic fuel. A co-solvent or a phase solubilizer, or a conjugated acetylene (e.g., 1,4-dicyclopropyl-1,3-butadiene) may also be present.

L4 ANSWER 3 OF 24 CAPLUS COPYRIGHT 2007 ACS on STN

AN 2002:577357 CAPLUS

DN 138:55672

TI Completely spirocyclopropanated macrocyclic oligodiacetylenes and their permethylated analogues: preparation and properties

AU De Meijere, Armin; Kozhushkov, Sergei I.

CS Institut fur Organische Chemie der Georg-August-Universitat Gottingen, Gottingen, 37077, Germany

SO Chemistry--A European Journal (2002); 8(14), 3195-3202

CODEN: CEUJED; ISSN: 0947-6539

PB Wiley-VCH Verlag GmbH

DT Journal

LA English

OS CASREACT 138:55672

AB The acyclic dehydrotrimer (I) and -hexamer (II) of 1,1-diethynyl-2,2,3,3-tetramethylcyclopropane were prepared from 1-chloro-1-(trimethylsilyl)ethynyl)-2,2,3,3-tetramethylcyclopropane in six and nine steps, resp., in 36 and 8% overall yield, using Cadiot-Chodkiewicz or Hay coupling procedures as key steps. Mono-tert-butyldimethylsilyl protection of the acyclic dehydrotrimer and -hexamer (III) of 1,1-diethynylcyclopropane followed by Hay coupling and desilylation furnished the acyclic dehydrohexamer III and -dodecamer (IV) in 35 and 56% overall yield, resp. Subsequent cyclizing oxidative dimerization of I or

cyclization of II using a modified Glaser protocol produced the first completely permethylspirocyclopropanated macrocyclic oligodiacetylene, (V) in 49 and 21% yield, resp. The cyclic dehydrohexa- (VI) and dehydrododecamer (VII) have been prepared from III and IV in 49 and 7% yield by applying the same protocol. VII is particularly interesting in that it contains 60 carbon atoms in the inner ring, and indeed a decomposition mode consecutively cleaving off ethylene units from it as well as from VI and tetramethylethylene from V has been proved by differential scanning calorimetry with evolved gas anal. The thermal decomposition of these exploding [6]rotanes VI and V set on at 100 and 135°C, resp., and release energies of 478 and 285 kcal·mol<sup>-1</sup>, resp., significantly more than the energy release of the explosive hexogen with 143 kcal mol<sup>-1</sup>.

RE.CNT 39 THERE ARE 39 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 4 OF 24 CAPLUS COPYRIGHT 2007 ACS on STN  
AN 2000:540665 CAPLUS  
DN 133:266292  
TI Synthesis of 1,3-Diynes via Palladium-Catalyzed Reaction of 1,1-Dibromo-1-alkenes  
AU Shen, Wang; Thomas, Sheela A.  
CS Department D4N6 Cancer Research Pharmaceutical Products Division, Abbott Laboratories, Abbott Park, IL, 60064-6101, USA  
SO Organic Letters (2000), 2(18), 2857-2860  
CODEN: ORLEF7; ISSN: 1523-7060  
PB American Chemical Society  
DT Journal  
LA English  
OS CASREACT 133:266292  
AB Both sym. and unsym. 1,3-diynes were prepared from the palladium-catalyzed reaction of 1,1-dibromo-1-alkenes. E.g., the Me 4-(2',2'-dibromovinyl)benzoate (I) undergoes homocoupling in up to 83% yield when a mixture of I (1.0 mmol), Pd2(dba)3, TFP (0.15 mmol), CuI (0.20 mmol), and Et3N (3 mmol) in DMF (3 mL) is flushed with N2 and heated at 90° for 4 h. The formation of sym. 1,3-diynes (homocoupling) was catalyzed by a weak ligand, tris(2-furyl)phosphine (TFP), and the addition of catalytic amount of CuI accelerated the reaction. The synthesis of unsym. 1,3-diynes (the Sonogashira reaction) required a highly electron rich tris(4-methoxyphenyl)phosphine as the ligand, and CuI promotes the formation of byproduct 1,1-diynyl-1-alkenes.

RE.CNT 35 THERE ARE 35 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 5 OF 24 CAPLUS COPYRIGHT 2007 ACS on STN  
AN 1999:74333 CAPLUS  
DN 130:202095  
TI Redox properties of functionalized fullerenes  
AU Boudon, Corinne; Gisselbrecht, Jean-Paul; Gross, Maurice; Cardullo, Francesca; Seiler, Paul; Isaacs, Lyle; Nierengarten, Jean-Francois; Haldimann, Richard F.; Diederich, Francois; Mordasini-Denti, Tiziana; Thiel, Walter  
CS Laboratoire d'electrochimie et de chimie physique du corps solide, C.N.R.S.-U.M.R. 7512 - Universite Louis Pasteur, Strasbourg, Fr.  
SO Canadian Journal of Chemical Engineering (1998), 76(6), 1008-1012  
CODEN: CJCEA7; ISSN: 0008-4034  
PB Canadian Society for Chemical Engineering  
DT Journal  
LA French  
AB The C60 phys. chemical properties make it possible to use it as an elemental base for the synthesis of new materials. As the functionalization of fullerenes modify these properties, the modifications of their phys. chemical properties, in particular their electrochem. properties have been studied for a series of highly functionalized fullerenes. This article presents the results obtained with the electrochem. studies of fullerenes C60 mono- and poly-functionalized covalently. Our objective was to analyze the

possible correlations between the redox properties of fullerenes and the degree, shape and nature of the functionalization. A series of functionalized fullerenes on positions [6,6] was synthesized to carry out the investigation. This unique series of mono- and poly-functionalized fullerenes provides an effective study of the modifications of the phys. chemical and electrochem. properties vs. the degree, shape and nature of the functionalization. The results obtained have been compared with literature data.

RE.CNT 32 THERE ARE 32 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 6 OF 24 CAPLUS COPYRIGHT 2007 ACS on STN  
AN 1998:223266 CAPLUS  
DN 128:316543  
TI A copper(I)-complexed rotaxane with two fullerene stoppers: synthesis, electrochemistry, and photoinduced processes  
AU Armaroli, Nicola; Diederich, Francois; Dietrich-Buchecker, Christiane O.; Flamigni, Lucia; Marconi, Giancarlo; Nierengarten, Jean-Francois; Sauvage, Jean-Pierre  
CS Istituto di Fotochimica e Radiazioni d'Alta Energia del CNR, Bologna, I-40129, Italy  
SO Chemistry--A European Journal (1998), 4(3), 406-416  
CODEN: CEUJED; ISSN: 0947-6539  
PB Wiley-VCH Verlag GmbH  
DT Journal  
LA English  
AB A rotaxane made from a bisphenanthroline Cu(I) complex and two C60 units acting as stoppers was synthesized. Electrochem., spectroscopic and photophys. properties of the individual components, a methanofullerene and a Cu(I) catenate, were determined. The properties of the methanofullerene were also compared with those of plain C60 and rationalized with the aid of semiempirical calcs. The changes in the photophys. properties detected in the rotaxane with respect to the models were assigned to the occurrence of intramol. processes. The excited singlet state localized on the fullerene and the MLCT excited state centered on the Cu(I) complex are both quenched. Deactivation of the fullerene excited singlet state occurs by energy transfer to the Cu(I)-complex moiety, which competes with intersystem crossing to triplet fullerene, whereas the Cu(I)-complex excited state is mainly quenched by electron transfer to form the charge-separated state consisting of the oxidized metal center [Cu(phen)2]2+ and the fullerene radical anion. The fullerene triplet, formed in reduced yield with respect to the model, is also quenched by electron transfer to the same charge-separated state. The ability of both model components to sensitize singlet oxygen is completely suppressed in the rotaxane. The occurrence of a fast back-electron-transfer reaction is postulated, as spectroscopic detection of the charge-separated state was not achieved.

RE.CNT 125 THERE ARE 125 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 7 OF 24 CAPLUS COPYRIGHT 2007 ACS on STN  
AN 1996:212770 CAPLUS  
DN 124:342817  
TI Fullerene-acetylene hybrids: towards a novel class of molecular carbon allotropes  
AU Timmerman, Peter; Anderson, Harry L.; Faust, Ruediger; Nierengarten, Jean-Francois; Habicher, Tilo; Seiler, Paul; Diederich, Francois  
CS Lab. Org. Chem., ETH-Zentrum, Zurich, CH-8092, Switz.  
SO Tetrahedron (1996), 52(14), 4925-47  
CODEN: TETRAB; ISSN: 0040-4020  
PB Elsevier  
DT Journal  
LA English  
OS CASREACT 124:342817  
AB The synthesis and complete characterization of 17 new fullerene-acetylene covalent derivs. is described. Reaction of 3-bromo-1,5-



bis(trimethylsilyl)penta-1,4-diyne with C60 gave bis-protected diethynylmethanofullerene (4) in 56% yield. Unsym. bis-protected diethynylmethanofullerene (6) was synthesized in 53% yield from tosylhydrazone [(i-Pr)<sub>3</sub>SiC.tplbond.CC(:NNHTos)C.tplbond.CSiMe<sub>3</sub>] and C60. Proto-desilylation of 4 and 6 gave the corresponding free alkynes (3 and 8) in 83% and 69% yield, resp. Partial deprotection of 4 afforded the mono-protected fullerene in 35% yield. Oxidative hetero-coupling reactions of 3 and 8 under Hay conditions with various monosubstituted acetylenes gave butadiynylmethanofullerenes (10-13) in yields varying from 25-49%. Homo-coupling of 8 produced dumbbell-shaped fullerene 14, the 1st dimeric fullerene that could be fully characterized. The x-ray crystal structure anal. of 14 revealed little or no electronic interaction between the two fullerene spheres. Addition of lithium trimethylsilylacetylide to C60 gave access to 1-substituted-2-(trimethylsilylethynyl)fullerenes. The acidity of hydro(trimethylsilylethynyl)fullerene (16), synthesized in 58% yield, was studied as a function of base and solvent. Reaction of lithiated (trimethylsilylethynyl)fullerene (17) with various electrophiles is discussed. Alc. (trimethylsilylethynyl)fullerenemethanol (25) was prepared in 57% yield by reaction of 17 with formaldehyde. Under strongly basic conditions, 25 eliminates formaldehyde to give 16 in quant. yield. Oxidation of 25 afforded (trimethylsilylethynyl)fullerenecarboxaldehyde in 53% yield, a rather unstable compound that is easily converted to hydrofullerene 16. Conversion of 25 to the corresponding tosylate could be performed in 40% yield.

L4 ANSWER 8 OF 24 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1995:834683 CAPLUS

DN 124:69578

TI Electrochemistry of mono- through hexakis-adducts of C60

AU Boudon, Corinne; Gisselbrecht, Jean-Paul; Gross, Maurice; Isaacs, Lyle; Anderson, Harry L.; Faust, Ruediger; Diederich, Francois

CS Faculte Chimie, Universite Louis Pasteur, Strasbourg, F-67008, Fr.

SO Helvetica Chimica Acta (1995), 78(5), 1334-44

CODEN: HCACAV; ISSN: 0018-019X

PB Verlag Helvetica Chimica Acta

DT Journal

LA English

AB The first systematic electrochem. study by cyclic voltammetry and rotating-disk electrode of the changes in redox properties of covalent fullerene derivs. as a function of increasing number of addends is reported. Dialkynylmethanofullerenes underwent multiple, fullerene-centered reduction steps at slightly more neg. potentials than C60. The 2 C-spheres in a butadiyne-linked, dumbbell-shaped dimeric fullerene derivative showed independent, identical redox characteristics. This highlights the insulating character of the sp<sup>3</sup>-C atoms in methanofullerenes which prevent through-bond communication of substituent effects from the methano bridge to the fullerene sphere. In a series of mono- through hexakis-adducts, formed by tether-directed remote functionalization, redns. became increasingly difficult and more irreversible with increasing number of addends. Whereas, in 0.1M Bu<sub>4</sub>NPF<sub>6</sub>/CH<sub>2</sub>Cl<sub>2</sub>, the first reduction of the mono-adduct occurred reversibly at -1.06 V vs. the ferrocene/ferricinium couple, the hexakis-adduct was reduced irreversibly only at -1.87 V. With incremental functionalization of the fullerene, the LUMO of the remaining conjugated framework is raised in energy. Reduction potentials were also dependent on the relative spatial disposition of the addends on the surface of the fullerene sphere. Observed UV/visible spectral changes and changes in the chemical reactivity were in accordance with the results of electrochem. measurements. The oxidation became more reversible with increasing number of addends. Whereas oxidns. were increasingly facilitated upon going from mono-adduct to tris-adduct (+1.22 and +0.90 V, resp.), they occur at nearly the same potential (+0.05-0.99 V) in the higher adducts. The oxidns. occurred in these compds. at a common sub-structural element, for which a cubic cyclophane structure is proposed. This sub-structure is fully developed in the hexakis-adduct.

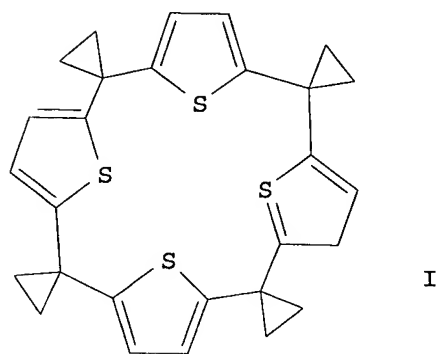
L4 ANSWER 9 OF 24 CAPLUS COPYRIGHT 2007 ACS on STN  
AN 1995:597863 CAPLUS  
DN 123:285269  
TI Synthesis of alkenyl- and alkynylcyclopropenes  
AU Haley, Michael M.; Biggs, Bluegrass; Looney, Will A.; Gilbertson, Robert D.  
CS Dep. of Chemistry, Univ. of Oregon, Eugene, OR, 97403, USA  
SO Tetrahedron Letters (1995), 36(20), 3457-60  
CODEN: TELEAY; ISSN: 0040-4039  
PB Elsevier  
DT Journal  
LA English  
OS CASREACT 123:285269  
AB Fluoride anion-promoted dehalosilation of 2-(chlorocyclopropyl)trimethylsilanes in the gas-phase was used to prepare a variety of monosubstituted cyclopropenes containing addnl. unsaturations. The cyclopropylsilanes were constructed easily from common intermediates. The dechlorination and desilylation of (2-chloro-3-ethynylcyclopropyl)trimethylsilane gave 3-ethynylcyclopropene. Dechlorination and desilylation of (2-chloro-3-ethynylcyclopropyl)trimethylsilane gave 3-ethynylcyclopropene. Thermal decomposition of 3-ethynylcyclopropene resulted in the formation of cyclopentadiene. Thermal decomposition of 3-ethynylcyclopropene resulted in the formation of 1,4-pentadiyne and 1,2-pentadien-4-yne.

L4 ANSWER 10 OF 24 CAPLUS COPYRIGHT 2007 ACS on STN  
AN 1995:580037 CAPLUS  
DN 123:256214  
TI Completely spirocyclopropanated macrocyclic oligodiacetylenes: the family of "exploding" [n]rotanes  
AU de Meijere, Armin; Kozhushkov, Sergei; Haumann, Thomas; Boese, Roland; Puls, Carsten; Cooney, Mark J.; Scott, Lawrence T.  
CS Inst. Org. Chemie, Georg-August-Univ., Goettingen, D-37077, Germany  
SO Chemistry--A European Journal (1995), 1(2), 124-31 Published in: Angew. Chem., Int. Ed. Engl., 34(9)  
CODEN: CEUJED; ISSN: 0947-6539  
PB VCH  
DT Journal  
LA English  
AB A general approach to the family of completely spirocyclopropanated macrocyclic polydiacetylenes, i.e., cyclic dehydrooligomers of 1,1-diethynylcyclopropane, was reported. The characterized examples of these [n]rotanes are for n = 5, 6, 7, 8, 9, 10, and 12. X-ray crystal structure analyses for the hydrocarbons with n = 5, 6, 7, and 8 disclose a strong electronic interaction between the cyclopropane and the acetylene units leading to a significant shortening of the distal and lengthening of the proximal cyclopropane bonds. While the five-sided compound can occur as a planar or envelope-shaped mol., depending on the solvent from which crystals are grown, the six-, seven-, and eight-sided mols. all have chair conformations. While the butadiyne units in the five-sided and six-sided compds. are bent slightly outwards, those in the seven- and eight-sided mols., resp., are bent distinctly inward. All these compds. are extremely high-energy mols.: when struck with a spatula or a pestle, they go off with a puff to yield black soot.

L4 ANSWER 11 OF 24 CAPLUS COPYRIGHT 2007 ACS on STN  
AN 1995:546520 CAPLUS  
DN 123:111642  
TI Fullerene-acetylene hybrids: path to new synthetic molecular carbon allotropes  
AU Anderson, Harry L.; Faust, Ruediger; Rubin, Yves; Diederich, Francois  
CS Lab. Organische Chem., ETH Zentrum Univ., Zurich, CH-8092, Switz.  
SO Angewandte Chemie (1994), 106(13), 1427-9  
CODEN: ANCEAD; ISSN: 0044-8249  
PB VCH  
DT Journal

LA German  
 OS CASREACT 123:111642  
 AB The synthesis of fullerene-acetylene derivs. was described.

L4 ANSWER 12 OF 24 CAPLUS COPYRIGHT 2007 ACS on STN  
 AN 1995:521991 CAPLUS  
 DN 123:33035  
 TI The reactivity of 1,3-butadiyne moieties in the "exploding" [n]rotanes - a crown of thiophenes  
 AU Kozhushkov, Sergei; Haumann, Thomas; Boese, Roland; Knieriem, Burkhardt; Scheib, Stefan; Baeuerle, Peter; de Meijere, Armin  
 CS Institut Oranische Chemie Universitaet Goettingen, Goettingen, D-37077, Germany  
 SO Angewandte Chemie, International Edition in English (1995), 34(7), 781-3  
 CODEN: ACIEAY; ISSN: 0570-0833  
 PB VCH  
 DT Journal  
 LA English  
 GI



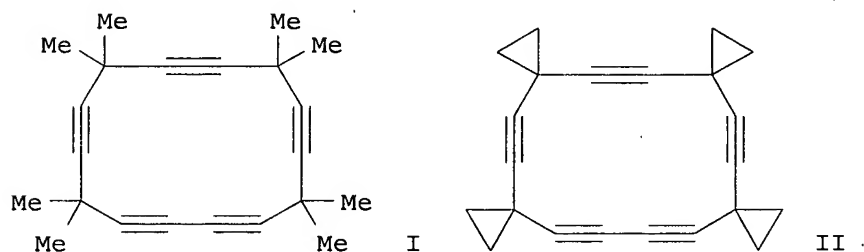
AB The thiophene crown compds. I [n = 2, 3, 4] were obtained by treating the corresponding diacetylenes with Na<sub>2</sub>S. The conformations of I are discussed.

L4 ANSWER 13 OF 24 CAPLUS COPYRIGHT 2007 ACS on STN  
 AN 1995:510099 CAPLUS  
 DN 122:305209  
 TI A copper(I)-complexed rotaxane with two fullerene stoppers  
 AU Diederich, Francois; Dietrich-Buchecker, Christiane; Nierengarten, Jean-Francois; Sauvage, Jean-Pierre  
 CS Lab. fuer Org. Chem., ETH-Zentrum, Zuerich, CH-8092, Switz.  
 SO Journal of the Chemical Society, Chemical Communications (1995), (7), 781-2  
 CODEN: JCCCAT; ISSN: 0022-4936  
 PB Royal Society of Chemistry  
 DT Journal  
 LA English  
 AB A three-component complex consisting of a coordinating ring, a copper(I) center and a difunctionalized fragment threaded inside the ring is reacted with a C<sub>60</sub> derivative to afford a soluble rotaxane with two fullerenes as stoppers in 15% yield.

L4 ANSWER 14 OF 24 CAPLUS COPYRIGHT 2007 ACS on STN  
 AN 1995:130752 CAPLUS  
 DN 122:159971  
 TI Enhancement of Through-Space and Through-Bond  $\pi$ -Orbital Interactions.

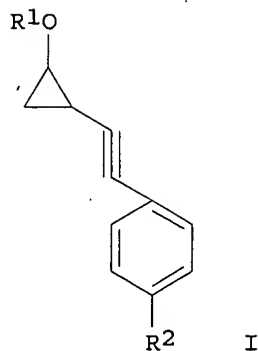
Syntheses and Properties of Permethylated and Perspirocyclopropanated  
Cyclotetradeca-1,3,6,9,12-pentayne

AU Scott, Lawrence T.; Cooney, Mark J.; Otte, Carola; Puls, Carsten; Haumann, Thomas; Boese, Roland; Smith, Amos B., III; Carroll, Patrick J.; de Meijere, Armin  
CS Department of Chemistry, Boston College, Chestnut Hill, MA, 02167-3860, USA  
SO Journal of the American Chemical Society (1994), 116(22), 10275-83  
CODEN: JACSAT; ISSN: 0002-7863  
DT Journal  
LA English  
OS CASREACT 122:159971  
GI



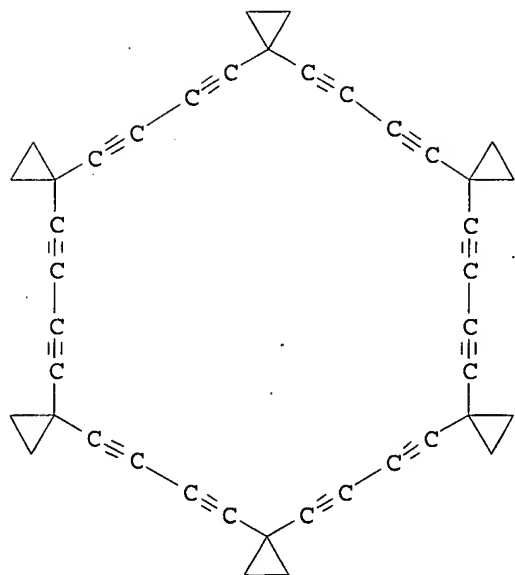
AB The permethylated and perspirocyclopropanated cyclotetradeca-1,3,6,9,12-pentaynes (I) and (II) have been synthesized and completely characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, UV, IR, and mass spectroscopy as well as by X-ray crystal structure anal. In the permethylated pentayne, compression of the internal C-C-C bond angles at the saturated carbon atoms flanking the diyne (103.8°) enhances the through-space  $\pi$ -orbital interactions and causes a bathochromic shift in the long wavelength UV absorption maximum ( $\lambda_{\text{max}}$  266 nm) relative to that of reference compds. ( $\lambda_{\text{max}}$  255-259 nm). In the perspirocyclopropanated pentayne, wider internal C-C-C bond angles at the corresponding carbon atoms (109.2°) reduce the through-space  $\pi$ -orbital interactions, but the through-bond  $\pi$ -orbital interactions are enhanced by spirocyclopropanation and cause a shift in the long wavelength UV absorption maximum to even longer wavelength ( $\lambda_{\text{max}}$  273 nm).

L4 ANSWER 15 OF 24 CAPLUS COPYRIGHT 2007 ACS on STN  
AN 1995:20353 CAPLUS  
DN 123:55394  
TI Cyclopropyl building blocks for organic synthesis. 25.  
Palladium(0)-catalyzed coupling reactions of 2-alkoxy-1-ethynylcyclopropanes with aryl and ethenyl halides: preparation of cyclopropyl substituted ethynylarenes, eneynes and enediynes  
AU McGaffin, Gregory; de Meijere, Armin  
CS Inst. fuer Org. Chem., Georg-August-Univ., Goettingen, D-37077, Germany  
SO Synthesis (1994), (6), 583-91  
CODEN: SYNTBF; ISSN: 0039-7881  
DT Journal  
LA English  
OS CASREACT 123:55394  
GI



AB 2-Alkoxy-1-ethynylcyclopropanes, readily available in diastereo- and enantiopure form, undergo facile palladium-catalyzed cross-coupling reactions with various mono- and oligohaloarenes, haloalkenes, and (E/Z)-1,2-dihalo-ethenes. The trans- and trans/cis-(2-alkoxycyclopropyl)ethynyl derivs., e.g. I (R1 = Et, Me3CSiMe2; R2 = H, Ph, 4-BrC6H4), were exclusively obtained in good to excellent yields. The coupling reaction thus opens the first direct access to configurationally uniform (2-alkoxycyclopropyl)ethynyl substituted arenes, and 2-alkoxycyclopropyl substituted eneynes and enediynes. Catalytic hydrogenation of ethynylarenes, e.g. I, smoothly afforded the corresponding (E/Z)-[(2-alkoxycyclopropyl)ethenyl]arenes, which are not directly accessible by palladium(0)-catalyzed coupling reactions of (E)-2-alkoxy-1-ethynylcyclopropanes with haloarenes.

L4 ANSWER 16 OF 24 CAPLUS COPYRIGHT 2007 ACS on STN  
 AN 1994:457031 CAPLUS  
 DN 121:57031  
 TI Hexaspiro[2.4.2.4.2.4.2.4.2.4.2.4]dotetraconta-  
 4,6,11,13,18,20,25,27,34,39.41-dodecayne, an exploding [6]rotane  
 AU de Meijere, Armin; Kozhushkov, Sergei; Puls, Carsten; Haumann, Thomas;  
 Boese, Roland; Cooney, Mark J.; Scott, Lawrence T.  
 CS Inst. Org. Che., Univ. Goettingen, Toettingen, D-37077, Germany  
 SO Angewandte Chemie (1994), 106(8), 934-6 (See also Angew. Chem., Int. Ed.  
 Engl., 1994, 33(8), 869-71)  
 CODEN: ANCEAD; ISSN: 0044-8249  
 DT Journal  
 LA German  
 GI



I

AB The title compound (I) was obtained together with the nonamer and an unidentified homolog from 1-trimethylsilylethynylcyclopropane. I catches fire on impact, leaving black soot.

L4 ANSWER 17 OF 24 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1992:621141 CAPLUS

DN 117:221141

TI Standard heats of formation of diacetylene derivatives

AU Luk'yanova, V. A.; Pimenova, S. M.; Timofeeva, L. P.; Kozina, M. P.; Kolesov, V. P.; Tarakanova, A. V.

CS Mosk. Gos. Univ., Moscow, Russia

SO Zhurnal Fizicheskoi Khimii (1992), 66(8), 2031-5

CODEN: ZFKHA9; ISSN: 0044-4537

DT Journal

LA Russian

AB The heats of combustion and of formation of 2,4-hexadiyne, 1-cyclopropyl-1,3-pentadiyne and 1,4-dicyclopropyl-1,3-butadiyne were determined. From these data, the effect of the triple bond was derived and the group contribution values were evaluated. The heat of formation of diacetylene was estimated.

L4 ANSWER 18 OF 24 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1992:40820 CAPLUS

DN 116:40820

TI Chromatographic characteristics of the retention of acetylene and cyclopropane derivatives on the polar liquid phase PEG-1500

AU Kotelnikova, T. A.; Garmash, A. V.; Ageev, E. P.

CS Mosk. Gos. Univ., Moscow, USSR

SO Vestnik Moskovskogo Universiteta, Seriya 2: Khimiya (1991), 32(3), 237-41

CODEN: VMUKA5; ISSN: 0579-9384

DT Journal

LA Russian

AB Gas chromatog. was used to determine the contribution of Me, CH<sub>2</sub>, C.tplbond.C, and cyclopropyl groups to the heat of solution of hydrocarbons in PEG-1500.

L4 ANSWER 19 OF 24 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1991:206627 CAPLUS

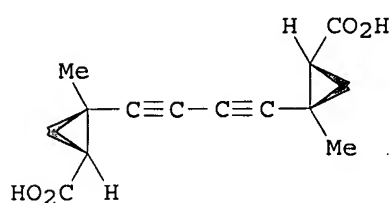
DN 114:206627

TI Cyclines. 9. Regioselective coupling of ethynylcyclopropane units: hexaspiro[2.0.2.4.2.0.2.4.2.0.2.4]triaconta-7,9,17,19,27,29-hexayne

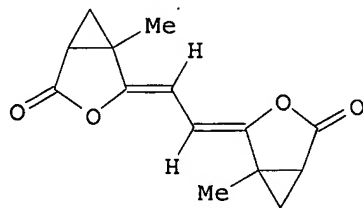
AU De Meijere, Armin; Jaekel, Frank; Simon, Arndt; Borrmann, Horst; Koehler, Jurgen; Johnels, Dan; Scott, Lawrence T.  
 CS Inst. Org. Chem., Univ. Hamburg, Hamburg, D-2000/13, Germany  
 SO Journal of the American Chemical Society (1991), 113(10), 3935-41  
 CODEN: JACSAT; ISSN: 0002-7863  
 DT Journal  
 LA English  
 OS CASREACT 114:206627  
 AB Regioselective synthetic methods are reported for the head-to-head, head-to-tail, and tail-to-tail coupling of ethynylcyclopropanes. Oxidative cyclization of the head-to-head dimer under high dilution conditions gave the title compound, an 18-membered macrocycle comprising 6 acetylenic units and 6 spirocyclopropanes that alternate pairwise around the ring. An x-ray crystal structure and spectroscopic properties of this novel macrocycle are reported.

L4 ANSWER 20 OF 24 CAPLUS COPYRIGHT 2007 ACS on STN  
 AN 1988:211429 CAPLUS  
 DN 108:211429  
 TI Heats of combustion and formation of some compounds with acetylene bonding  
 AU Pimenova, S. M.; Kozina, M. P.; Gal'chenko, G. L.; Siretskaya, T. V.; Takhistov, V. V.; Kuznetsova, T. S.; Proskurnina, M. V.; Kotel'nikova, T. A.  
 CS USSR  
 SO Termodinam. Organ. Soed., Gor'kii (1986) 12-16  
 From: Ref. Zh., Khim. 1987, Abstr. No. 23B3025  
 DT Journal  
 LA Russian  
 AB Title only translated.

L4 ANSWER 21 OF 24 CAPLUS COPYRIGHT 2007 ACS on STN  
 AN 1981:550298 CAPLUS  
 DN 95:150298  
 TI Formation of unsaturated bicyclic  $\gamma$ -butyrolactone in the oxidative dimerization of 2-methyl-2-ethynylcyclopropanecarboxylic acid  
 AU Shapiro, E. A.; Lun'kova, G. V.; Shteinshneider, A. Ya.; Dolgii, I. E.; Nefedov, O. M.  
 CS Inst. Org. Khim. im. Zelinskogo, Moscow, USSR  
 SO Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya (1981), (5), 1164-6  
 CODEN: IASKA6; ISSN: 0002-3353  
 DT Journal  
 LA Russian  
 GI



I



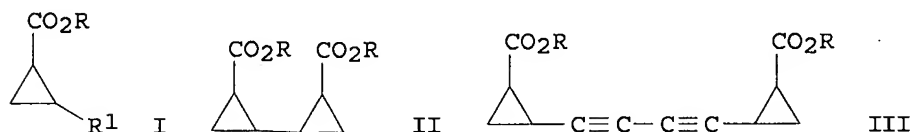
II

AB The title reaction on a mixture of cis and trans isomers in the presence of CuCl and NH<sub>4</sub>Cl gave 53% diacetylene I and 14% dilactone II. II was probably formed by intramol. cyclization of I.

L4 ANSWER 22 OF 24 CAPLUS COPYRIGHT 2007 ACS on STN  
 AN 1979:557317 CAPLUS  
 DN 91:157317  
 TI Formation of 2-vinylcyclopropanecarboxylic acid esters in reactions of alkyl diazoacetates with gaseous butadiene and synthesis of

2-ethynylcyclopropanecarboxylic acid from them

AU Dolgii, I. E.; Shapiro, E. A.; Nefedov, O. M.  
CS Inst. Org. Khim. Zelinskogo, Moscow, USSR  
SO Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya (1979), (6), 1282-6  
CODEN: IASKA6; ISSN: 0002-3353  
DT Journal  
LA Russian  
OS CASREACT 91:157317  
GI



AB Treatment of butadiene with  $\text{N}_2\text{CHCO}_2\text{R}$  ( $\text{R} = \text{Me}, \text{Et}$ ) at atmospheric pressure in the

presence of  $\text{CuSO}_4$  or  $\text{CuO}$  gave cis- and trans-I ( $\text{R}^1 = \text{vinyl}$ ), II, and  $\text{RO}_2\text{CCH}:\text{CHCO}_2\text{R}$ . I ( $\text{R}^1 = \text{vinyl}$ ) and addnl.  $\text{N}_2\text{CHCO}_2\text{R}$  in the presence of  $\text{CuSO}_4$  gave II. Bromination of I ( $\text{R}^1 = \text{vinyl}$ ) gave I ( $\text{R}^1 = \text{CHBrCH}_2\text{Br}$ ), which were dehydrobrominated to I ( $\text{R}^1 = \text{C.tplbond.CH}$ ); the latter were oxidized to III.

L4 ANSWER 23 OF 24 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1965:468252 CAPLUS

DN 63:68252

OREF 63:12536f-h

TI N.M.R. (nuclear magnetic resonance) spectra of substituted cyclopropanes

AU Vo-Quang, Liliane; Simonnin, Marie Paule

CS Ecole Natl. Super. Chim., Paris, Fr.

SO Bulletin de la Societe Chimique de France (1965), (5), 1534-8

CODEN: BSCFAS; ISSN: 0037-8968

DT Journal

LA French

GI For diagram(s), see printed CA Issue.

AB The spectra of 9 tetrasubstituted derivs. of I, where  $\text{R} = (1) \text{C.tplbond.CH}$ ,  $(2) (\text{C.tplbond.C})_2$  (doubled mol.),  $(3) \text{C.tplbond.CCO}_2\text{H}$ ,  $(4) \text{C.tplbond.CC.tplbond.CCH}_2\text{Ph}$ , and  $(5) \text{Ac}$ , and the X are both Cl or both Br (the Br of (3) is excluded) were recorded at 60 Mc. Coupling consts. were measured either on the pure liquids or solns. of different concns. in  $\text{CCl}_4$  or  $\text{DCCl}_3$  and chemical shifts were determined at infinite dilution in  $\text{CCl}_4$  with respect to  $\text{Me}_4\text{Si}$ . In all cases the proton lines were at lower field strengths for the dibromides, which is contrary to expectation, since Cl is more electroneg. than Br. For a given substituent,  $\delta\text{A}-\delta\text{B}$  was independent of the nature of the halogen and virtually constant at 0.32-0.35 ppm. when the radical was acetylenic, but increased to 0.95 ppm. for the ketone. Chemical shifts and the 3 coupling consts. were also obtained for II and III. Differences in the 2 spectra are considered in relation to the stereochemistry of the 2 isomers.

L4 ANSWER 24 OF 24 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1965:445837 CAPLUS

DN 63:45837

OREF 63:8222g-h,8223a-h,8224a-c

TI Dihaloethynylcyclopropane

AU Vo-Quang, Liliane; Cadiot, Paul

CS Ecole Natl. Super. Chim., Paris

SO Bulletin de la Societe Chimique de France (1965), (5), 1418-24

CODEN: BSCFAS; ISSN: 0037-8968

DT Journal

LA French



GI For diagram(s), see printed CA Issue.

AB Phenylacetylene and 1-hexyne did not react with dichlorocarbenes, but with the enynes  $\text{CH}_2\text{:}-\text{CMeC.tplbond.CH}$  (I) and II, selective attack occurred at the double bond to give dihaloethynylcyclopropanes (III) with yields of 55-62% for the chlorine derivs, and 50-66% for the corresponding bromides. The dihalocarbenes prepared by reaction of  $\text{CHCl}_3$  or  $\text{CHBr}_3$  on a strong base in pentane (Doering and Hoffmann, CA 49, 15805b) were used to obtain the following compds.: 2,2-dichloro-1-ethynyl-1-methylcyclopropane (IV) from I as a colorless oil, b<sub>20</sub> 52° yield 65%, purity by measurement of acetylenic H (K<sub>2</sub>HgI<sub>4</sub> method) 95%; 2,2-dibromo-1-ethynyl-1-methylcyclopropane (V) from I as a colorless oil, reddening rapidly in air (distilled under N), b<sub>24</sub> 83°, yield 56%, purity (K<sub>2</sub>HgI<sub>4</sub>) 98.8%; 7,7-dichloro-1-ethynylbicyclo[4.1.0]heptane (VI) from II as a pale yellow oil, turning brown in air, b<sub>10</sub> 99°, yield 55%, purity (AgNO<sub>3</sub>) 98%; 7,7-dibromo-1-ethynylbicyclo[4.1.0]heptane (VII) from II as a colorless oil, reddening in air (distilled under N), b<sub>5</sub> 130°, yield 49.9%, purity (K<sub>2</sub>HgI<sub>4</sub>) 95%; 2,2-dichloro-1-ethynyl-1-ethyl-3-methylcyclopropane (VIII) from 3-ethyl-3-penten-1-yne (cis-trans) as a pale yellow oil, b<sub>1869</sub>°, yield 42.5%, purity (K<sub>2</sub>HgI<sub>4</sub>) 98.9%; 6,6-dichloro-1-ethynylbicyclo[3.1.0]hexane (IX) from ethynylcyclopentane as a pale yellow oil rapidly turning brown in air, b<sub>10</sub> 89-90°, yield 35.5%, purity (K<sub>2</sub>HgI<sub>4</sub>) 95%. The best yields were obtained using a temperature of 0° and a reaction time of 3 hrs. Good yields (59-65%) were also obtained when the dihalocarbenes were prepared by reaction between K tert-butyrate and Et trichloroacetate (Parham and Schwelzer, CA 55, 11328b) after increasing the reaction time to 8 hrs. at 0° but the thermal decarboxylation of Na trichloroacetate in a neutral solvent (dimethoxyethane) gave disappointing yields (18-22%). The compds. of type III showed the usual reactions of materials containing acetylenic H. Thus, X in ether with CO<sub>2</sub> under pressure readily gave XI. EtMgBr was prepared from 6.5 g. EtBr, 1.5 g. Mg, and 50 ml. anhydrous ether, and then 0.05 mole of the dichloroethynylcyclopropane in 20 ml. ether was added and refluxing continued 30 min. The reaction mixture, containing X, was poured rapidly into an autoclave, dry ice added, and the autoclave quickly closed. Efficient agitation was maintained 24 hrs. and the autoclave contents then poured into a mixture of ice and HCl, XI being finally removed with 50 ml. 10% ammonia. This aqueous solution was then acidified with HCl and reextd. with ether. The residue was dried, concentrated, and recrystd. The following compds. were obtained in this way: (2,2-dichloro-1-methyl-1-cyclopropyl)propionic acid (XII) from IV, m. 81° (water), yield 66%, purity (from acidity) 99.4%; 7,7-dichlorobicyclo[4.1.0]hept-1-ylpropionic acid (XIII) from VI, m. 90° (petroleum ether), yield 42%, purity 99%. Reaction of XIV with true acetylenic hydrocarbons according to the method of Chodkiewicz (CA 52, 14565c) gave directly sym. (XV) and unsym. (XVI) conjugated diynes. XIV was obtained by dissolving 0.1 mole III in 4 ml. N-methylpyrrolidone and cooling to -5°. NaOBr prepared from 5.5 ml. Br and 30 ml. 10N NaOH was then added in small amts. The mixture was agitated vigorously for 30 min. and it became progressively more milky as the bromide formed. The latter was extracted with ether and excess NaOBr destroyed by addition of NH<sub>4</sub>Cl solution until the ether layer was colorless. XIV after concentration and extraction was used without further purification for the preparation of the following sym. conjugated diynes: bis(2,2-dichloro-1-methyl-cyclopropyl)1,4-butadiyne from the bromo derivative of 1,1-dichloro-2-ethynyl-2-methylcyclopropane (XVII), m. 92°, yield 49%; bis(2,2-dibromo-1-methyl-cyclopropyl)-1,4-butadiyne from the dibromo analog of XVII as pink crystals, m. 110°, yield 64%; 1,4-bis[7,7-dichlorobicyclo[4.1.0]heptyl]butadiyne from the bromo derivative of VI. The crude material was an oil which was crystallized from dilute EtOH and then recrystd. from pure EtOH to give white crystals, yellowing in air, m. 130°, yield 53.2%. 1,4-Bis(7,7-dibromobicyclo[4.1.0]heptyl)butadiyne from the bromo derivative of VII. The crude material was an oil only crystallized with difficulty to a grayish-brown powder which decomposed rapidly

in air, m. 140° (decomposition) (pure EtOH), yield 35%. The unsym. conjugated diynes were obtained in similar manner. To a concentrated solution

of

2.28 g. propargyl anthracene in tetrahydrofuran was added 0.01 mole crude XIV. After addition of 0.1 g. KBr, the mixture was extracted with ether and

the

crude product, after concentration and drying, was purified on Al<sub>2</sub>O<sub>3</sub> (eluant benzene) and recrystd. from petroleum ether or ligroine. The following compds. were obtained: 1-(2,2-dichloro-1-methyl-1-cyclopropyl)-5-(9-anthryl)-pentadiyne as golden-yellow platelets, m. 191° (petroleum ether), yield 78%; 1-(2,2-dibromo-1-methyl-1-cyclopropyl)-5-(9-anthryl)-pentadiyne as clear yellow platelets, m. 185° (petroleum ether), yield 48.5%; 1-(7,7-dichlorobicyclo[4.1.0]-1-heptyl)-5-(anthryl)pentadiyne as a pale yellow powder, m. 182° (ligroine), yield 67.5%; 1-[7,7-dibromobicyclo[4.1.0]-1-heptyl]-5-(9-anthryl)pentadiyne as a golden-yellow powder rapidly turning brown in air, m. 170° (ligroine), yield 25%. The compds. of type III were also easily hydrated to give acetyldihalocyclopropanes (XVIII). After refluxing 0.05 mole III in 100 ml. MeOH with 5 ml. of a solution of HgSO<sub>4</sub> (prepared previously from 0.5 g. HgO, 1 ml. concentrated H<sub>2</sub>SO<sub>4</sub>, and 10 ml. H<sub>2</sub>O) 2 hrs., the mixture was extracted

with ether and the organic phase distilled. The following ketones of type XVIII were obtained: 1-acetyl-2,2-dichloro-1-methylcyclopropane from IV, b<sub>17</sub> 73.5°, yield 54%; 1-acetyl-2,2-dibromo-1-methylcyclopropane from V as a colorless oil, reddening rapidly in air, b<sub>20</sub> 104°, yield 64%; 1-acetyl-7,7-dichlorobicyclo[4.1.0]heptane from IV as a colorless oil, b<sub>1</sub> 98°, yield 60.5%; 1-acetyl-7,7-dibromobicyclo[4.1.0]heptane from V as a viscous liquid reddening rapidly in air, b<sub>0.5</sub> 105°, yield 24.8%. V treated with MeLi was converted into a mixture of cis and trans isomers (with respect to Br and CH<sub>3</sub>) of 2-bromo-1-ethynyl-1-methylcyclopropane (XIX and XX). V (24 g.) was introduced drop by drop into a solution containing 0.4 mole MeLi in 200 ml. anhydrous ether maintained

at

-20 to -30°. The reaction was carried out under N with shaking continued for 30 min. at this temperature. After hydrolysis the ethereal extract

was dried over Na<sub>2</sub>SO<sub>4</sub> and several successive distns. then gave a mixture of XIX and XX, b<sub>12</sub> 38°, yield of mixture 50%. They are not stable in the reaction medium, the relative proportion of the two isomers decreasing as the reaction temperature was raised. As the reaction progressed further V was transformed into a series of more volatile compds. among which XXI was identified. Chromatographic separation gave a 17% yield of the cis isomer and a 33% yield of the trans. The structures of the various compds. are generally confirmed by ir and uv spectroscopic examination. 38 references.

=>

---Logging off of STN---

=>

Executing the logoff script...

=> LOG Y

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

68.39

240.70

DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)

SINCE FILE

TOTAL

ENTRY

SESSION

CA SUBSCRIBER PRICE

-18.72

-18.72